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<p>(54) Title: HIGH ACTIVITY CATALYSTS FOR THE PREPARATION OF POLYETHYLENE WITH AN INTERMEDIATE MOLECULAR WEIGHT DISTRIBUTION</p> <p>(57) Abstract</p> <p>A supported alpha-olefin polymerization catalyst composition of this invention of improved activity as measured by productivity is prepared in a multi-step process. An ethylene homopolymerization or ethylene copolymerization catalyst is formed by: (i) providing a slurry of a solid porous inorganic support having reactive hydroxyl (-OH) groups and a non-polar solvent; (ii) impregnating said support having -OH groups, with RMgR' compound, to form an intermediate, which intermediate has an -OH group:Mg ratio of less than 1, wherein each of said R and R' is alkyl of 1 to 12 carbon atoms and is the same or different; (iii) treating the intermediate with TiCl₄ to form a titanium containing intermediate which has an -OH group:Ti ratio of less than 1; (iv) reacting the titanium containing intermediate with an amount of oxygen containing electron donor containing 1 to 15 carbon atoms, combining the electron donor treated titanium containing intermediate with triethylaluminum to form the catalyst. The catalyst also produces polymers having relatively intermediate molecular weight distribution.</p>		

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HIGH ACTIVITY CATALYSTS
FOR THE PREPARATION OF POLYETHYLENE
WITH AN INTERMEDIATE MOLECULAR WEIGHT DISTRIBUTION

The present invention relates to a method for
5 polymerizing alpha-olefins, a catalyst for such a
polymerization method and a method for producing such a
catalyst. In particular, the present invention relates to a
catalyst, and a method for preparation thereof, which
produces high density polyethylene or linear low density
10 polyethylene (LLDPE) having an intermediate molecular weight
distribution, as evidenced by relatively intermediate values
of melt flow ratio (MFR), suitable for film applications.
The invention is also directed to a highly productive
polymerization process carried out with the catalyst of the
15 invention.

In commercial applications, ethylene homopolymers and
ethylene/1-olefin copolymers with either a very narrow
molecular weight distribution (MWD) or very broad MWD are
important. However, recently polymer with intermediate MWDs
20 have been found to be important for blending two or more
polymer samples into commercially important products, e.g.,
for film or blow-molding applications.

The two or more polymer samples which are blended into
the final product each may have a very different molecular
25 weight. One polymer sample will usually have a relatively
very high molecular weight as indicated by a High Load Melt
Index (HLMI) of 0.4 - 5, while the other polymer sample will
have a relatively very low molecular weight as indicated by a
Melt Index (MI) of 20-1000. These polymer samples may be
30 prepared separately in individual polymerization reactors or
may be prepared in tandem polymerization reactors where the
relatively high and low molecular weight fractions are
prepared sequentially in the polymerization process.

One of the measures of the molecular weight distribution
35 of the resin is melt flow ratio (MFR), which is the ratio of

high load melt index (HLMI or I_{21}) to melt index (I_2) for a given resin. The melt flow ratio is believed to be an indication of the molecular weight distribution of the polymer, the higher the value, the broader the molecular weight distribution. Resins having relatively very low MFR values, e.g., of 15 to 30, have relatively narrow molecular weight distribution. Additionally, resins with relatively high MFR values (i.e. 80-150) are said to have a relatively broad MWD. Resins with an intermediate MWD have MFR values of 30-70.

Many catalyst systems exhibit a tendency to produce resins with very low MFR values. For example, Allen et al, U.S. Patent No. 4,732,882, discloses an alpha-olefin polymerization catalyst composition activated with trimethylaluminum which produces polymers having relatively very low values of MFR and low hexane extractables. A catalyst composition capable of producing ethylene homopolymers or ethylene/1-olefin copolymers containing up to 10 mol% 1-olefin having relatively an intermediate molecular weight distribution, i.e., MFRs of 30-70, a high activity catalyst with relatively good flow index response [flow index response refers to the ability of a catalyst to produce relatively lower molecular weight polymer than the polymer produced by another catalyst under the same polymerization conditions].

A supported alpha-olefin polymerization catalyst composition of this invention of improved activity as measured by productivity is prepared in a multi-step process.

An ethylene homopolymerization or ethylene copolymerization catalyst is formed by:

- (i) providing a slurry in a non-polar solvent of a solid porous inorganic support having reactive hydroxyl groups;
- (ii) impregnating said support having hydroxyl groups, (Formula I) with RMgR' compound, to form an intermediate, which intermediate has an Mg/hydroxyl group ratio of greater than 1,

wherein each of said R and R' is alkyl of 1 to 12 carbon atoms and is the same or different;

(iii) treating the intermediate with TiCl_4 to form a titanium containing intermediate which has a Ti/Mg ratio of greater than 0.5; and

(iv) reacting the titanium containing intermediate with an oxygen containing electron donor compound containing 1 to 15 carbon atoms; combining the electron donor treated titanium containing intermediate with triethylaluminum to form the catalyst. The catalyst also produces polymers having relatively an intermediate molecular weight distribution, high activity and good Flow Index response.

The polymers prepared in the presence of the catalyst composition of this invention are linear polyethylenes with short chain branching which are homopolymers of ethylene or copolymers of ethylene and higher alpha-olefins. The polymers exhibit relatively intermediate values of melt flow ratio (MFR), as compared to similar polymers prepared in the presence of previously-known catalyst compositions. Thus, the polymers prepared with the catalyst compositions of the invention are especially suitable as components for the production of resins used in film and blow molding applications.

Catalysts produced according to the present invention are described below in terms of the manner in which they are made.

Catalyst Synthesis

The carrier material is a solid, particulate, porous, preferably inorganic material. These carrier materials include inorganic materials, such as oxides of silicon and/or aluminum. The carrier material is used in the form of a dry powder having an average particle size of from 1 micron to 250 microns, preferably from 10 microns to 150 microns. The carrier material is also porous and has a surface area of at least 3 square meters per gram (m^2/gm), and preferably at least 50 m^2/gm . The carrier material should be dry, that is,

free of absorbed water. Drying of the carrier material can be effected by heating at 100° to 1000°C, preferably at 600°C. When the carrier is silica, it is heated at at least 200°C, preferably 200° to 850°C and most preferably at 600°C. The carrier material must have at least some active hydroxyl (OH) groups to produce the catalyst composition of this invention.

In the most preferred embodiment, the carrier is silica which, prior to the use thereof in the first catalyst synthesis step, has been dehydrated by fluidizing it with nitrogen and heating at 600°C for 16 hours to achieve a surface hydroxyl group concentration of 0.7 millimoles per gram (mmols/gm). The silica of the most preferred embodiment is a high surface area, amorphous silica (surface area = 300 m²/gm; pore volume of 1.65 cm³/gm), and it is a material marketed under the tradenames of Davison 952 or Davison 955 by the Davison Chemical Division of W. R. Grace and Company. The silica is in the form of spherical particles, e.g., as obtained by a spray-drying process.

The carrier material is slurried in a non-polar solvent and the resulting slurry is contacted with at least one organomagnesium composition having the empirical formula (I). The slurry of the carrier material in the solvent is prepared by introducing the carrier into the solvent, preferably while stirring, and heating the mixture to 25° to 100°C, preferably to 40° to 60°C. The slurry is then contacted with the aforementioned organomagnesium composition, while the heating is continued at the aforementioned temperature.

The organomagnesium composition has the empirical formula $R_m Mg R'_n$ where R and R' are the same or different C₄-C₁₂ alkyl groups, preferably C₄-C₁₀ alkyl groups, more preferably C₄-C₈ normal alkyl groups, and most preferably both R and R' are butyl groups, and m and n are each 0, 1 or 2, providing that m + n is equal to the valence of Mg.

Suitable non-polar solvents are materials in which all of the reactants used herein, i.e., the organomagnesium composition ($R_m Mg R'_n$) transition metal compound, and the

oxygen containing electron donor compound are at least partially soluble and which are liquid at reaction temperatures herein. Preferred non-polar solvents are alkanes, such as isopentane, hexane, n-heptane, octane, nonane, and decane, although a variety of other materials including cycloalkanes, such as cyclohexane, aromatics, such as benzene and ethylbenzene, may also be employed. The most preferred non-polar solvent is hexane. Prior to use, the non-polar solvent should be purified, such as by percolation through silica gel and/or molecular sieves, to remove traces of water, oxygen, polar compounds, and other materials capable of adversely affecting catalyst activity.

In the most preferred embodiment of the synthesis of this catalyst it is important to add only such an amount of the organomagnesium composition that will be deposited, physically or chemically, onto the support since any excess of the organomagnesium composition in the solution may react with other synthesis chemicals and precipitate outside of the support. The carrier drying temperature affects the number of sites on the carrier available for the organomagnesium composition - the higher the drying temperature the lower the number of sites. Thus, the exact molar ratio of the organomagnesium composition to the hydroxyl groups will vary and must be determined on a case-by-case basis to assure that only so much of the organomagnesium composition is added to the solution as will be deposited onto the support without leaving any excess of the organomagnesium composition in the solution.

Furthermore, it is believed that the molar amount of the organomagnesium composition deposited onto the support is greater than the molar content of the hydroxyl groups on the support. Thus, the molar ratios given below are intended only as an approximate guideline and the exact amount of the organomagnesium composition in this embodiment must be controlled by the functional limitation discussed above, i.e., it must not be greater than that which can be deposited

onto the support. If greater than that amount is added to the solvent, the excess may react with the other compounds used in the preparation thereby forming a precipitate outside of the support which is detrimental in the synthesis of our catalyst and must be avoided. The amount of the organo-magnesium composition which is not greater than that deposited onto the support can be determined in any conventional manner, e.g., by adding the organomagnesium composition to the slurry of the carrier in the solvent, while stirring the slurry, until the organomagnesium composition is detected as a solution in the solvent.

For example, for the silica carrier heated at 600°C, the amount of the organomagnesium composition added to the slurry is such that the molar ratio of Mg to the hydroxyl groups (OH) on the solid carrier is 1:1 to 3:1, preferably 1.1:1 to 2:1, more preferably 1.2:1 to 1.8:1 and most preferably 1.4:1. The organomagnesium composition dissolves in the non-polar solvent to form a solution from which the organo-magnesium composition is deposited onto the carrier.

It is also possible to add such an amount of the organomagnesium composition which is in excess of that which will be deposited onto the support, and then remove, e.g., by filtration and washing, any excess of the organomagnesium composition. However, this alternative is less desirable than the most preferred embodiment described above.

After organomagnesium compound addition, the slurry is contacted with at least one transition metal compound soluble in the non-polar solvent. This synthesis step is conducted at 25° to 75°C, preferably at 30° to 65°C, and most preferably at 40° to 55°C. In a preferred embodiment, the amount of the transition metal compound added is not greater than that which can be deposited onto the carrier. The exact molar ratio of Mg to the transition metal and of the transition metal to the hydroxyl groups of the carrier will therefore vary (depending, e.g., on the carrier drying temperature) and must be determined on a case-by-case basis. For example, for

the silica carrier heated at 200° to 850°C, the amount of the transition metal compound is such that the molar ratio of the transition metal, derived from the transition metal compound, to the hydroxyl groups of the carrier is 1 to 2.0, preferably 1.2 to 1.8. The amount of the transition metal compound is also such that the molar ratio of Mg to the transition metal is 0.5 to 3, preferably 1 to 2. It was found that these molar ratios produce a catalyst composition which produces resins having relatively intermediate melt flow ratio values of 30 to 60.

Suitable transition metal compounds used herein are compounds of metals of Groups 4 and 5 of the Periodic Chart of the Elements, as published by Chemical and Engineering News, 63(5), 27, 1985, providing that such compounds are soluble in the non-polar solvents. Non-limiting examples of such compounds are titanium and vanadium halides, e.g., titanium tetrachloride, TiCl_4 , vanadium tetrachloride, VCl_4 , vanadium oxytrichloride, VOCl_3 , titanium and vanadium alkoxides, wherein the alkoxide moiety has a branched or unbranched alkyl radical of 1 to 20 carbon atoms, preferably 1 to 6 carbon atoms. The preferred transition metal compounds are titanium compounds, preferably tetravalent titanium compounds. The most preferred titanium compound is titanium tetrachloride.

Mixtures of such transition metal compounds may also be used and generally no restrictions are imposed on the transition metal compounds which may be included. Any transition metal compound that may be used alone may also be used in conjunction with other transition metal compounds.

Oxygen-containing electron donors used in the catalyst synthesis are of the formula R_1COOR_2 and $\text{R}_3\text{-O-R}_4$, or $\text{R}_4\text{-OH}$, respectively. R_1 and R_2 may be the same or different and each can contain 1 to 15 carbon atoms. Each of R_1 and R_2 may be alkyl, aryl, alkyl substituted aryl; R_3 and R_4 may be the same or different and each can contain 1 to 15 carbon atoms and may be alkyl, aryl, alkyl substituted aryl or aryl

substituted alkyl, or alkylene; comprehended by this definition is that R_3 and R_4 together may form alkylene groups thereby defining R_3OR_4 as a cyclic ether. Preferred oxygen containing electron donors include p-cresol, methanol, ethyl benzoate, tetrahydrofuran, and n-butyl ether. Most preferably, the oxygen containing electron donor is ethyl benzoate, tetrahydrofuran or n-butylether.

Preferably the electron donor is an ester or an ether which is added to the catalyst synthesis after transition metal addition to the synthesis slurry. The electron donors (ED) are added in amounts, effective to increase the productivity of the catalyst and its selectivity for polymers produced with MFRs ranging from 30 to 60 at HLMI ranging from 0.1 to 40,000. Practically, such amounts range from a Ti/ED molar ratio of 0.5 to 2.0.

The non-polar solvent is slowly removed, e.g., by distillation or evaporation after precursor formation. The temperature at which the non-polar solvent is removed from the synthesis mixture affects the productivity of the resulting catalyst composition. Lower solvent removal temperatures produce catalyst compositions which are substantially more active than those produced with higher solvent removal temperatures. For this reason, it is preferred to remove the non-polar solvent at 40° to 65°C, preferably at 45° to 55°C and most preferably at 55°C by drying, distillation or evaporation or any other conventional means.

The resulting free-flowing powder, referred to herein as a catalyst precursor, is combined with an organoaluminum activator. The combination of the precursor of this invention with the triethylaluminum as an activator produces an alpha-olefin polymerization catalyst composition having very high activity. The activator is used in an amount which is at least effective to promote the polymerization activity of the solid catalyst component of this invention. The amount of the activator is sufficient to give an Al:Ti molar

ratio of 15:1 to 1000:1, preferably 20:1 to 300:1, and most preferably 25:1 to 100:1.

Without wishing to be bound by any theory of operability, it is believed that the catalyst composition of this invention is produced by chemically impregnating the support with catalyst components sequentially added to the slurry of the carrier in the non-polar solvent. Therefore, all of the catalyst synthesis chemical ingredients must be soluble in the non-polar solvent used in the synthesis. The order of addition of the reagents may also be important since the catalyst synthesis procedure is predicated on the chemical reaction between the chemical ingredients sequentially added to the non-polar solvent (a liquid) and the solid carrier material or a catalyst intermediate supported by such a material (a solid). Thus, the reaction is a solid-liquid reaction. For example, the catalyst synthesis procedure must be conducted in such a manner as to avoid the reaction of two or more reagents in the non-polar solvent to form a reaction product insoluble in the non-polar solvent outside of the pores of the solid catalyst support. Such an insoluble reaction product would be incapable of reacting with the carrier or the catalyst intermediate and therefore would not be incorporated onto the solid support of the catalyst composition.

The catalyst precursors of the present invention are prepared in the substantial absence of water, oxygen, and other catalyst poisons. Such catalyst poisons can be excluded during the catalyst preparation steps by any well known methods, e.g., by carrying out the preparation under an atmosphere of nitrogen, argon or other inert gas. An inert gas purge can serve the dual purpose of excluding external contaminants during the preparation and removing undesirable reaction by-products resulting from the preparation of the neat, liquid reaction product. Purification of the non-polar solvent employed in the catalyst is also helpful in this regard.

The catalyst may be activated in situ by adding the activator and catalyst separately to the polymerization medium. It is also possible to combine the catalyst and the activator before the introduction thereof into the polymerization medium, e.g., for up to 2 hours prior to the introduction thereof into the polymerization medium at a temperature of from -40° to 100°C.

Polymerization

Ethylene homopolymers or ethylene/1-olefin copolymers are polymerized with the catalysts prepared according to the present invention by any suitable process. Such processes include polymerizations carried out in suspension, in solution or in the gas phase. Gas phase polymerization reactions are preferred, e.g., those taking place in stirred bed reactors and, especially, fluidized bed reactors.

The molecular weight of the polymer may be controlled in a known manner, e.g., by using hydrogen. With the catalysts produced according to the present invention, molecular weight may be suitably controlled with hydrogen when the polymerization is carried out at relatively low temperatures, e.g., from 30° to 105°C. This control of molecular weight may be evidenced by measurable positive change in melt index (I_2) of the polymer produced.

The molecular weight distribution of the polymers prepared in the presence of the catalysts of the present invention, as expressed by the MFR values, varies from 30 to 60, preferably 32 to 50. As is known to those skilled in the art, such MFR values are indicative of a relatively intermediate molecular weight distribution of the polymer. As is also known to those skilled in the art, such MFR values are indicative of the polymers especially suitable as components for polymers used for film or blow molding applications. MFR is defined herein as the ratio of the high

load melt index (HLMI or I_{21}) divided by the melt index, i.e.,

$$\text{MFR} = \frac{I_{21}}{I_2}$$

5

Lower MFR values indicate relatively narrow molecular weight distribution polymers.

The catalysts prepared according to the present invention are highly active and may have an activity of at least 1 to 5 kilograms of polymer per gram of catalyst per 100 psi of ethylene in 1 hour.

The polyethylene polymers prepared in accordance with the present invention are homopolymers of ethylene or copolymers of ethylene with one or more C_3 - C_{10} alpha-olefins. Thus, copolymers having two monomeric units are possible as well as terpolymers having three monomeric units. Particular examples of such polymers include ethylene/1-butene copolymers, ethylene/1-hexene copolymers, ethylene/1-octene copolymers, ethylene/4-methyl/1-pentene copolymers, ethylene/1-butene/1-hexene terpolymers, ethylene/propylene/1-hexene terpolymers and ethylene/propylene/1-butene terpolymers.

The polyethylene polymers produced in accordance with the present invention preferably contain at least 80 percent by weight of ethylene units.

A particularly desirable method for producing polyethylene polymers according to the present invention is in a fluid bed reactor. Such a reactor and means for operating it are described by Levine et al, U.S. Patent No. 4,011,382, Karol et al, U.S. Patent 4,302, 566 and by Nowlin et al, U.S. Patent 4,481,301, the entire contents of all of which are incorporated herein by reference. The polymer produced in such a reactor contains the catalyst particles because the catalyst is not separated from the polymer.

Preferably, in accordance with this invention, bimodal ethylene polymer blends having a desirable combination of

processability and mechanical properties are produced by a process including the steps of polymerizing gaseous monomeric compositions comprising a major proportion of ethylene in at least two gas phase, fluidized bed reactors operating in the tandem mode under the following conditions. In the first reactor, a gas comprising monomeric composition and, optionally, a small amount of hydrogen, is contacted under polymerization conditions with a catalyst of the invention, at a hydrogen/ethylene molar ratio of no higher than 0.3 and an ethylene partial pressure no higher than 100 psia such as to produce a relatively high molecular weight (HMW) polymer powder wherein the polymer is deposited on the catalyst particles. The HMW polymer powder containing the catalyst is then transferred to a second reactor with, optionally, additional activator (or cocatalyst) which may be the same or different from the cocatalyst utilized in the first reactor but with no additional transition metal catalyst component, together with a gaseous mixture comprising hydrogen and monomeric composition wherein additional polymerization is carried out at a hydrogen/ethylene molar ratio of at least 0.9, the ratio being sufficiently high such that it is at least 8.0 times that in the first reactor, and an ethylene partial pressure at least 1.7 times that in the first reactor, to produce a relatively low molecular weight (LMW) polymer much of which is deposited on and within the HMW polymer/catalyst particles from the first reactor, such that the fraction of HMW polymer in the bimodal polymer leaving the second reactor is at least 0.35.

The foregoing conditions provide for a process wherein the production of fines tending to foul compressors and other equipment is kept to a relatively low level. Moreover, such conditions provide for an inhibited level of productivity in the first reactor with a resulting increased level of productivity in the second reactor to produce a bimodal polymer blend having a favorable melt flow ratio (MFR, an indication of molecular weight distribution) and a high

degree of homogeneity (indicated by low level of gels and low heterogeneity index) caused by a substantial degree of blending of HMW and LMW polymer in each final polymer particle inherently resulting from the process operation.

- 5 The bimodal blend is capable of being processed without undue difficulty into films and containers for household industrial chemicals having a superior combination of mechanical properties.

10 The gaseous monomer entering both reactors may consist wholly of ethylene or may comprise a preponderance of ethylene and a minor amount of a comonomer such as a alpha-olefin containing 3 to 10 carbon atoms. The comonomer may be present in the monomeric compositions entering either or both reactors.

- 15 In many cases, the monomer composition will not be the same in both reactors. For example, in making resin intended for high density film, it is preferred that the monomer entering the first reactor contain a minor amount of comonomer such as 1-hexene so that the HMW component of the
20 bimodal product is a copolymer, whereas the monomer fed to the second reactor consists essentially of ethylene so that the LMW component of the product is substantially an ethylene homopolymer. When a comonomer is employed so as to obtain a desired copolymer in either or both reactors, the molar ratio
25 of comonomer to ethylene may be in the range, for example, of 0.005 to 0.7, preferably 0.04 to 0.6.

- Hydrogen may or may not be used to modulate the molecular weight of the HMW polymer made in the first reactor. Thus, hydrogen may be fed to the first reactor such
30 that the molar ratio of hydrogen to ethylene (H_2/C_2 ratio) is, for example, up to 0.3, preferably 0.005 to 0.2. In the second reactor it is necessary to produce a LMW polymer with a low enough molecular weight and in sufficient quantity so as to produce a bimodal resin which can be formed, with a
35 minimum of processing difficulties, into end use products such as films and containers for household industrial

chemicals having a superior combination of mechanical properties. For this purpose, hydrogen is fed to the second reactor with the ethylene containing monomer such that the hydrogen to ethylene mole ratio in the gas phase is 0.9, preferably in the range of 0.9 to 5.0 and most preferably in the range of 1.0 to 3.5. Moreover, to provide a sufficient difference between the molecular weights of the polymers in the first and second reactor so as to obtain a bimodal resin product having a wide enough molecular weight distribution necessary for the desired levels of processability and mechanical properties, the hydrogen to ethylene mole ratios in the two reactors should be such that the ratio in the second reactor is at least 8.0 times the ratio in the first reactor, for example in the range 8.0 to 10,000 times such ratio, and preferably 10 to 200 times the ratio in the first reactor.

Utilizing the hydrogen to ethylene ratios set out previously to obtain the desired molecular weights of the HMW and LMW polymers produced in the first and second reactors respectively tends to result in relatively high polymer productivity in the first reactor and relatively low productivity in the second reactor. This tends to result in turn in a bimodal polymer product containing too little LMW polymer to maintain satisfactory processability. A significant part of this invention lies in the discovery that this effect can be largely overcome by employing ethylene partial pressures in the two reactors so as to reduce the polymer productivity in the first reactor and raise such productivity in the second reactor. For this purpose, the ethylene partial pressure employed in the first reactor is no higher than 100 psia, for example in the range of 15 to 100 psia, preferably in the range of 20 to 80 psia and the ethylene partial pressure in the second reactor is, for example in the range of 26 to 170 psia, preferably 45 to 120 psia, with the ethylene partial pressures in any specific process being such that the ratio of ethylene partial

pressure in the second to that in the first reactor is 1.7, preferably 1.7 to 7.0, and more preferably 2.0 to 4.0.

If desired for any purpose, e.g., to control superficial gas velocity or to absorb heat of reaction, an inert gas such as nitrogen may also be present in one or both reactors in addition to the monomer and hydrogen. Thus the total pressure in both reactors may be in the range, for example, of 100 to 600 psig, preferably 200 to 350 psig.

The temperature of polymerization in the first reactor may be in the range, for example, of 60° to 130°C, preferably 60° to 90°C, while the temperature in the second reactor may be in the range, for example, of 80° to 130°C, preferably 90° to 120°C. For the purpose of controlling molecular weight and productivity in both reactors, it is preferred that the temperature in the second reactor be at least 10°C higher, preferably 30° to 60°C higher than that in the first reactor.

The residence time of the catalyst in each reactor is controlled so that the productivity is suppressed in the first reactor and enhanced in the second reactor, consistent with the desired properties of the bimodal polymer product. Thus, the residence time may be, for example, 0.5 to 6 hours, preferably 1 to 3 hours in the first reactor, and, for example, 1 to 12 hours, preferably 2.5 to 5 hours in the second reactor, with the ratio of residence time in the second reactor to that in the first reactor being in the range, for example, of 5 to 0.7, preferably 2 to 1.

The superficial gas velocity through both reactors is sufficiently high to disperse effectively the heat of reaction so as to prevent the temperature from rising to levels which could partially melt the polymer and shut the reactor down, and high enough to maintain the integrity of the fluidized beds. Such gas velocity is in the range, for example, of 40 to 120, preferably 50 to 90 cm/sec.

The productivity of the process in the first reactor in terms of grams of polymer per gram atom of transition metal in the catalyst multiplied by 10^6 , may be in the range, for

example, of 1.6 to 16.0, preferably 3.2 to 9.6; in the second reactor, the productivity may be in the range, for example, of 0.6 to 9.6, preferably 1.6 to 3.5, and in the overall process, the productivity is in the range, for example, of 2.2 to 25.6, preferably 4.8 to 16.0. The foregoing ranges are based on analysis of residual catalyst metals in the resin product.

The polymer produced in the first reactor has a flow index (FI or I_{21} , measured at 190°C in accordance with ASTM D-1238, Condition F), for example, of 0.05 to 5, preferably 0.1 to 3 grams/10 min. and a density in the range, for example, of 0.890 to 0.960, preferably 0.900 to 0.940 grams/cc.

The polymer produced in the second reactor has a melt index (MI or I_2 , measured at 190°C in accordance with ASTM D-1238, Condition E) in the range, for example, of 10 to 4000, preferably 15 to 2000 grams/10 min. and a density in the range, for example, of 0.890 to 0.976, preferably 0.930 to 0.976 grams/cc. These values are calculated based on a single reactor process model using steady state process data.

The final granular bimodal polymer from the second reactor has a weight fraction of HMW polymer of at least 0.35, preferably in the range of 0.35 to 0.75, more preferably 0.45 to 0.65, a flow index in the range, for example, of 3 to 200, preferably 6 to 100 grams/10 min., a melt flow ratio (MFR, calculated as the ratio of flow index to melt index) in the range, for example, of 60 to 250, preferably 80 to 150, a density in the range, for example, of 0.89 to 0.965, preferably 0.910 to 0.960, an average particle size (APS) in the range, for example, of 127 to 1270, preferably 380 to 1100 microns, and a fines content (defined as particles which pass through a 120 mesh screen) of less than 10 wt.%, preferably less than 3 wt.%. With regard to fines content, it has been found that a very low amount of fines are produced in the first (HMW) reactor and that the percentage of fines changes very little across the second

reactor. This is surprising since a relatively large amount of fines are produced when the first or only reactor in a gas phase, fluidized bed system issued to produce a relatively low molecular weight (LMW) polymer as defined herein. A
5 probable explanation for this is that in the process of this invention, the LMW polymer formed in the second reactor deposits primarily within the void structure of the HMW polymer particles produced in the first reactor, minimizing the formation of LMW fines. This is indicated by an increase
10 in settled bulk density (SBD) across the second reactor while the APS stays fairly constant.

When pellets are formed from granular resin which was stabilized and compounded with two passes on a Brabender extruder to ensure uniform blending, such pellets have a flow
15 index in the range, for example, of 3 to 200, preferably 6 to 100 grams/10 min., a melt flow ratio in the range, for example, of 60 to 250, preferably 80 to 150, and a heterogeneity index (HI, the ratio of the FI's of the granular to the pelleted resin) in the range for example of
20 1.0 to 1.5, preferably 1.0 to 1.3. HI indicates the relative degree of inter-particle heterogeneity of the granular resin.

The following examples further illustrate the essential features of the invention. However, it will be apparent to those skilled in the art that the specific reactants and
25 reaction conditions used in the Examples do not limit the scope of the invention.

EXAMPLE 1

Catalyst Preparation:

All manipulations were conducted under a nitrogen
30 atmosphere by using standard Schlenk techniques. Into a 200 ml Schlenk flask was placed 7.0 grams of Davison grade 955 silica, which was previously dried under a nitrogen purge at 600°C for 16 hours. Hexane (90 ml) was added to the silica. Dibutylmagnesium (7.0 mmol) was added to the stirred slurry
35 at 50° to 55°C and stirring was continued for one hour. TiCl_4 (7.0 mmol) was added to the reaction flask (50° to

55°C) and stirring was continued for one hour. An electron donor (7.0 mmol) was then added to the flask (50° to 55°C) and stirring was continued for an additional hour. Hexane was then removed by distillation with a nitrogen purge at 50°
 5 to 55°C. Yield varied from 8.4-9.3 grams depending on the electron donor employed.

Polymerization:

Ethylene/1-hexene copolymers were prepared with these catalysts under the same polymerization conditions. A
 10 typical example is shown below. A 1.6 liter stainless steel autoclave under a slow nitrogen purge at 50°C was filled with 750 ml of dry hexane, 30 ml of dry 1-hexene, and 3.0 mmol of triethylaluminum. The reactor was closed, the stirring was increased to 900 rpm, and the internal temperature was
 15 increased to 85°C. The internal pressure was raised 12 psi with hydrogen. Ethylene was introduced to maintain the pressure at 120 psi. The internal temperature was decreased to 80°C, 20.0 mg of catalyst was introduced into the reactor with ethylene over pressure, and the internal temperature was
 20 increased and held at 85°C. The polymerization was continued for 60 minutes, and then the ethylene supply was stopped and the reactor was allowed to cool to room temperature. The polyethylene was collected and air dried.

Given below are the productivities, flow indexes, and
 25 melt flow ratios of the catalysts prepared according to the sequence.

	DBM SiO ₂	TiCl ₄	Electron Donor		
			Productivity*	Melt Index	Flow Index
30 Ex.	Electron Donor			(I ₂)	(I ₂ 1)
1 ^{xx}	None (Control)	590	0.03	2.4	70.1
2	p-cresol	1120	0.13	5.1	39.8
3	methanol	1150	0.08	3.5	43.4
35 4	ethyl benzoate	2250	0.19	5.7	30.5
5	tetrahydrofuran	2720	0.16	6.0	36.4
6	n-butyl ether	2780	0.22	6.9	31.3

* Productivity is given in units of gram polyethylene per gram of catalyst-hr-100 psi ethylene.

xx Comparative

The data show that the incorporation of an electron donor
5 substantially increases the productivity of the catalyst. Using
ether as an electron donor (Examples 5 and 6) produced catalysts
with the highest productivities. Thus, tetrahydrofuran and n-
butyl ether were comparable electron donors. An ester (ethyl
benzoate) electron donor yielded a catalyst with slightly lower
10 productivity while the alcohol and substituted phenol electron
donor catalysts were less active than the ether electron donor
catalysts. The polymer produced by the catalysts of the
invention exhibit an intermediate molecular weight distribution
as indicated by MFR values between 30-45 and a lower molecular
15 weight as indicated by higher melt index (12) values. Hence,
the catalysts have better melt index response than the
comparative catalyst.

CLAIMS:

1. In an ethylene homopolymerization or ethylene
copolymerization catalyst which controls the molecular weight
distribution of polymer product as determined by MFR, wherein
5 the catalyst is formed by

(i) providing a slurry of a solid porous inorganic support
having reactive (-OH) groups and a non-polar solvent;

(ii) impregnating said support having -OH groups, with
RMgR' compound, to form an intermediate, which intermediate has
10 an -OH group:Mg ratio of less than 1,

wherein each of said R and R' is alkyl of 1 to 12 carbon
atoms and is the same or different and wherein RMgR' is soluble
in said non-polar solvent;

wherein the amount of the RMgR' used in said step (i) is
15 such that the molar ratio Mg:OH is 1:1 to 3:1,

(iii) treating the intermediate with TiCl_4 to form a
titanium containing intermediate which has an -OH group:Ti ratio
of less than 1;

wherein the amount of the TiCl_4 present in said step (iii)
20 is such that the molar ratio of Mg to Ti is 0.5 to 2, the
improvement comprising:

(iv) reacting the titanium containing intermediate with an
oxygen containing electron donor containing 2 to 15 carbon
atoms; combining the electron donor treated titanium containing
25 intermediate with triethylaluminum;

wherein said electron donor is present in an amount effective to provide a molar ratio of titanium(metal):electron donor of 0.5 to 2, and

wherein said determined MFR ranges from 30 to 60 at an HLMI of 0.1 to 40000.

2. A catalyst composition of claim 2, wherein R and R' are C₄-C₈ alkyl groups.

3. A catalyst composition of claim 2, wherein the amount of the TiCl₄ present in said step (iii) is such that the molar ratio of Mg:Ti is 1 to 1.5.

4. A catalyst composition of claim 3, wherein the amount of the RMgR' used in said step (i) is such that the molar ratio Mg:OH is 1.1:1 to 2:1.

5. A catalyst composition of claim 4, wherein the solid, porous carrier is silica which, prior to contact thereof with the solvent in step (i), is heated at a temperature of at least 200°C.

6. A catalyst composition of claim 5, wherein the silica has, after the heating, surface hydroxyl groups concentration of 0.7 mmoles/gr, a surface area of 300 m²/gram and a pore volume of 1.65 m³/gram.

7. An ethylene homopolymerization or copolymerization
process which comprises contacting a feed comprising ethylene,
under ethylene homopolymerization or copolymerization conditions
with the catalyst of claim 1 to the molecular weight
5 distribution of polymer product as determined by MFR.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/11078

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 31/26, 31/32

US CL :502/110, 111, 115

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/110, 111, 115

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,727,049 A (FURUHASHI et al.) 23 February 1988, see column 7 and example 6.	1-7
X	US 4,301,029 A (CAUNT et al.) 17 November 1981, see column 7 and example 70.	1-7

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search	Date of mailing of the international search report
14 AUGUST 1997	30.10.97

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INTERNATIONAL SEARCH REPORT

information on patent family members

Intern. Application No.

PCT/IT 97/00161

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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FR 2628993 A	29-09-89	NONE	

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IT 97/00161

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B22D11/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B22D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 546 206 A (NIPPON STEEL CORP) 16 June 1993 cited in the application see column 4, line 39 - column 7, line 18; figures 1,2	1-9
A	EP 0 692 330 A (USINOR SACILOR ; THYSSEN STAHL AG (DE)) 17 January 1996 see column 4, line 49 - column 8, line 40; figures 1,2	1-9
A	EP 0 698 433 A (USINOR SACILOR ; THYSSEN STAHL AG (DE)) 28 February 1996 see claims 1-8; figures 1-3	1-9
A	FR 2 628 993 A (IRSID) 29 September 1989 see claims 1-7; figures 1-4	7

☐ Further documents are listed in the continuation of box C.

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